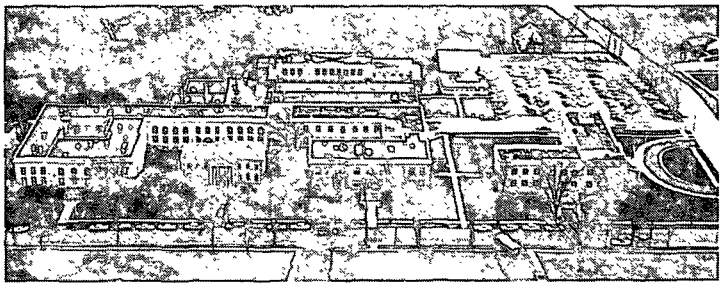

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NUCLEOPHILICITIES OF PULPING REAGENTS (I): REACTIONS WITH AN UNSATURATED CARBON CENTER

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NUCLEOPHILICITIES OF PULPING REAGENTS (I): REACTIONS WITH AN UNSATURATED CARBON CENTER

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ABSTRACT

The rate of isomerization of cis- to trans-cinnamic acid in water at 195°C was monitored as a function of added nucleophile. The observed order of anthrahydroquinone ion > hydrosulfide ion ≈ hydroxide ion is believed to be related to relative nucleophilicities of these ions toward a conjugated unsaturated carbon center. The expected addition products (adducts) were not observed but could be synthesized and, when subjected to the reaction conditions, rapidly converted to trans-cinnamic acid.

INTRODUCTION

The nucleophilicity of an ion is not an intrinsic property, but depends on the type of substrate under attack, the type of solvent used in the reaction, and the reaction temperature.[1] At room temperature, hydrosulfide ion is seven times more reactive than hydroxide ion with methyl bromide (a saturated carbon site).[2] However, hydroxide ion is a stronger nucleophile than hydrosulfide ion toward a carbonyl carbon (an unsaturated carbon site). Polarizability of the nucleophile is important during reactions at a saturated carbon center, while basicity is important during reactions at an unsaturated carbon center.[3,4,5]

Solvation of the nucleophile is a key factor in determining reactivity. Nucleophilic reactions typically proceed much faster in dipolar aprotic solvents than in polar solvents.[6] In the gas phase, where absolute reaction rates are very high, oxyanions are more nucleophilic than sulfur analogs toward both saturated carbon centers[7,8] and unsaturated carbon centers.[9] Hydration of hydroxide ion with up to three water molecules in gas phase reactions causes a drop in reactivity with methyl bromide of 4 orders of magnitude. There is a further difference of 12 orders of magnitude between the hydrated (three water molecules) gas phase and solution phase cases.[10] The effects of solvation on nucleophilic properties of ions in water at high temperatures (170-200°C) is not known, but would be expected to be somewhere between room temperature water solutions and gas phase conditions.

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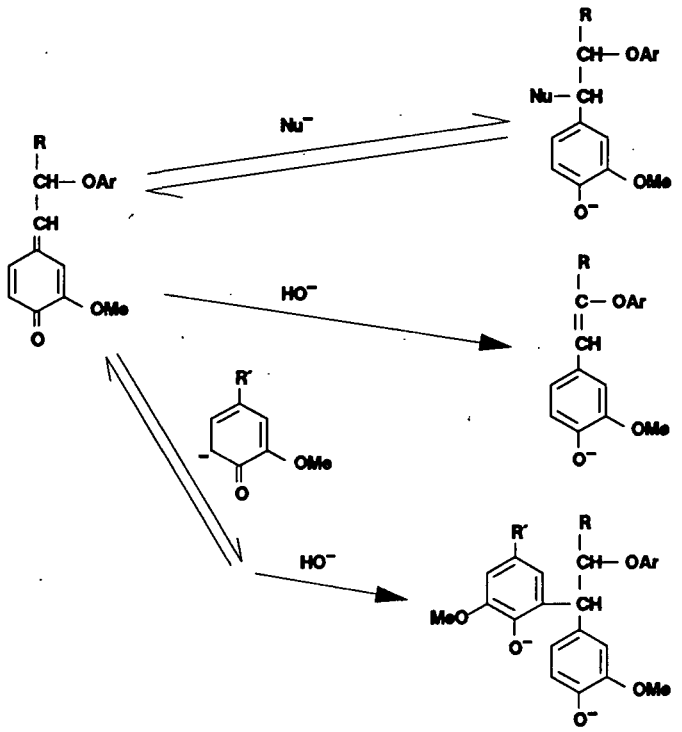
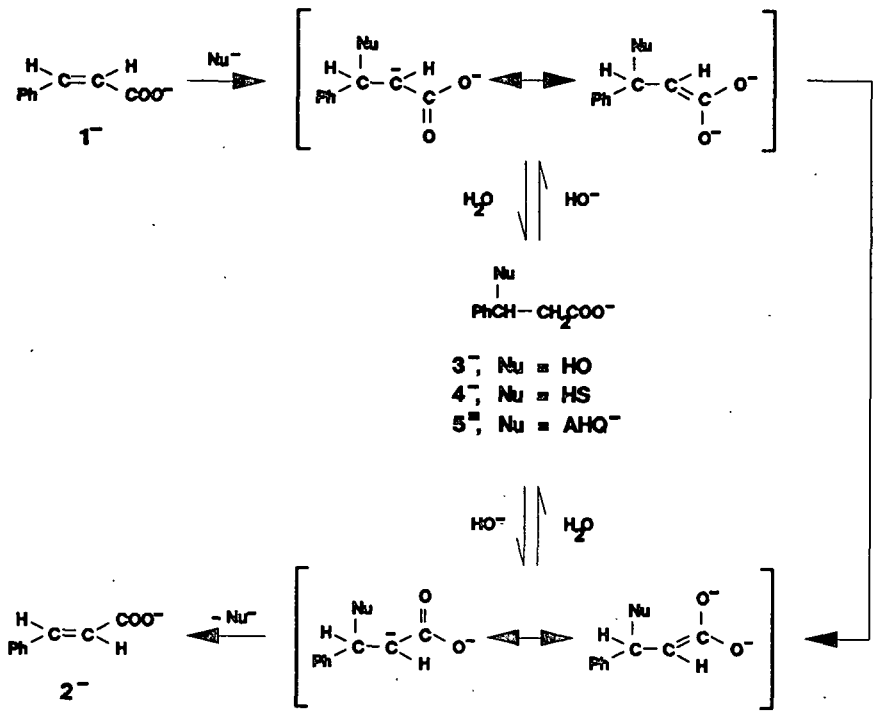
Chemical pulping involves heating wood chips in water at 170°C in the presence of high levels of sodium hydroxide; the goal is to free the carbohydrate fibers from the lignin component. Delignification is aided by hydrosulfide ion (kraft process) and anthrahydroquinone ion (AQ process). These ions, including hydroxide ion, have been proposed to promote pulping because of their nucleophilic character.[11] Yet, nucleophilicities of these species at 170°C in water have not been systematically studied.

An important step in the delignification of wood is the addition of the pulping nucleophile to a lignin quinonemethide;[11] this formal Michael reaction is shown in Eq. 1. The addition step appears to be reversible.[12] The addition product (adduct) can undergo fragmentation reactions which cause the lignin to dissolve. There are several competing reactions occurring with the quinonemethides: deprotonation by HO^- to relatively stable styrene products (Eq. 2), condensation reactions with phenolate ions (Eq. 3), and electron transfer reactions which lead to rearomatization. At least one pulping reagent, anthrahydroquinone ion (AHQ^{-2}), can function both as a nucleophile or as an electron transfer agent.[13]



While we would prefer to study nucleophilic addition reactions to quinonemethides, their great reactivity and abundant competing reactions would limit the extent of useful conclusions which could be drawn. Therefore, we chose to study cis-cinnamic acid as a model of a quinonemethide. cis-Cinnamic acid (1) has an unsaturated conjugated carbonyl reaction site, similar to the C_α reaction site in quinonemethides, and should be susceptible to Michael addition reactions. The carboxylate group in cis-cinnamic acid imparts solubility in basic solutions. The expected addition-elimination reactions of nucleophiles should cause 1 to rearrange to the less sterically crowded trans-cinnamic acid (2) without many competing reactions (Scheme 1). The isomerization of cis- to trans-cinnamic acid has been shown to occur through an addition-elimination mechanism under acidic conditions[14] and under high temperature alkaline conditions.[15]

SCHEME 1



The conversion of cis-cinnamic acid to trans-cinnamic acid is a multi-step reaction. In order for this compound to be a suitable model for investigating

nucleophilic addition, the slow step should be the addition step. If either rearrangement or elimination is the slow step, the resulting rate constant will probably not reflect the nucleophilicity of the reagent. This report concerns the high temperature reactions of cis-cinnamic acid with various nucleophiles.

RESULTS AND DISCUSSION

Product Studies

The isomerization of 1 was investigated in oxygen-free water solutions which contained hydroxide, hydrosulfide, and anthrahydroquinone ions. Temperatures of 195°C were employed to get reasonable reaction rates. The reactions were followed using gas chromatographic (GC) techniques. The identity of each product was confirmed by comparing its GC and GC-mass spectrometric (GC-MS) properties to a synthesized or purchased sample.

Compound 1 was heated in aqueous alkaline sodium hydroxide at 195°C to simulate soda pulping reactions. The major product was trans-cinnamic acid (2). The anticipated reaction scheme is outlined in Scheme 1, $Nu^- = HO^-$. Hydroxide ion can add to the double bond to produce an adduct (3^{-2}). Protonation, deprotonation and elimination of hydroxide ion from the adduct could lead to the trans isomer 2; alternatively, the initial adduct 3^{-2} may simply undergo a bond rotation about C_α-C_β and then eliminate hydroxide ion to give trans-cinnamic acid.

A mass balance, obtained by adding the observed amounts of cis- and trans-cinnamic acids and comparing the amount to the starting levels of each, was quite good (Fig. 1). Small amounts of benzaldehyde and benzoic acid, identified by GC-MS, probably are responsible for the small decrease in the material balance at longer reaction times. Both by-products were also formed by heating trans-cinnamic acid in aqueous sodium hydroxide.

The intermediate adduct 3 was not detected. However, when a synthesized sample of compound 3 was heated at 195°C in an aqueous sodium hydroxide, trans-cinnamic acid was rapidly formed. Based on these results, it was concluded that the slow step was the addition step rather than the elimination step.

cis-Cinnamic acid (1) was also isomerized to trans-cinnamic acid (2) in aqueous sodium sulfide at 195°C to simulate kraft pulping reactions. The

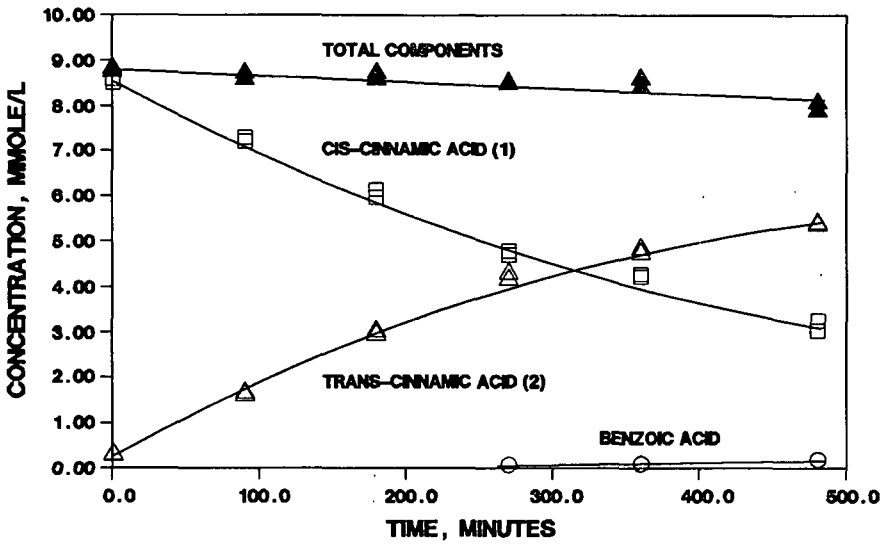


Figure 1. Mass balance for the reaction of 1 in 0.78M at 195°C.

expected reaction pathways are a combination of those for Nu^- = HO^- and HS^- shown in Scheme 1. Under the conditions employed, sodium sulfide is effectively hydrolyzed to one molecule of sodium hydrosulfide and one molecule of sodium hydroxide (Eq. 4).[16]

$$Na_2S + H_2O \longrightarrow NaSH + NaOH \qquad (4)$$

Hydrosulfide ion can add to the carbon-carbon double bond to produce adduct 4^- which can then either rearrange or be protonated and deprotonated and then eliminate hydrosulfate ion to form **2**. The intermediate sulfur adduct **4** was not detected by GC-MS; an authentic sample of **4** was found to rapidly degrade to trans-cinnamic acid under the employed reaction conditions. The material balance was nearly constant (Fig. 2). Benzaldehyde and benzoic acid were again present in small amounts.

When cis-cinnamic acid was reacted in solutions containing high concentrations (> 1M) of sodium hydroxide or sulfide, hydrocinnamic acid was also observed as a product. The reactions, therefore, were studied at lower base concentrations to minimize by-product formation and maximize conversion to **2**. The mechanism by which hydrocinnamic acid is formed was not investigated.

Compound **1** was heated in solutions containing hydroxide and anthrahydroquinone ions to simulate soda-AQ pulping reactions at 195°C. The major product of the reaction was trans-cinnamic acid (**2**). The anticipated reaction scheme is

a combination of those for Nu^- = HO^- and AHQ^{2-} shown in Scheme 1. Anthrahydroquinone ion may add to the double bond in 1 to produce intermediate adduct 5^- which then can either rearrange or be protonated and deprotonated and then eliminate anthrahydroquinone ion to form trans-cinnamic acid. Adduct 5 was not observed in the reaction mixture. An authentic sample of 5 was not stable under the employed reaction conditions and was rapidly converted to 2.

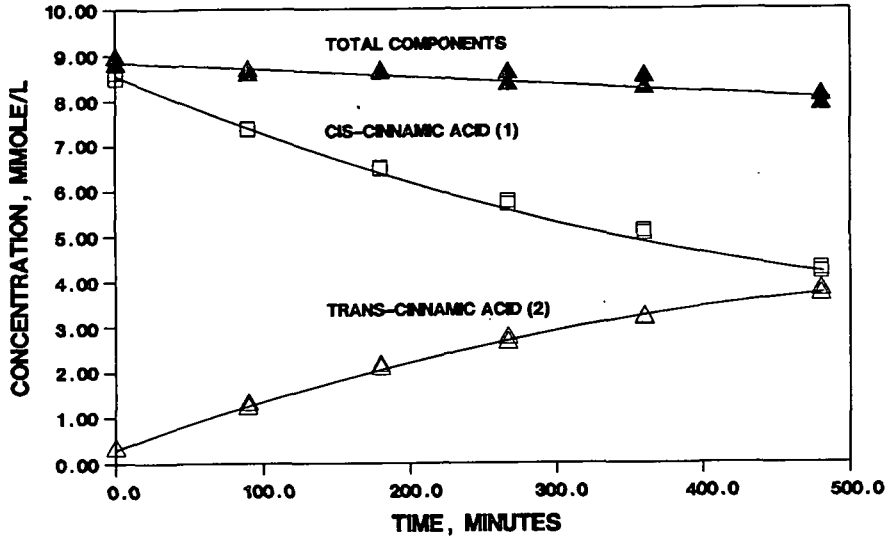


Figure 2. Mass balance for the reaction of 1 in 0.38M NaOH and 0.393M NaSH at 195°C.

The material balance was not as complete (Fig. 3) as previous reactions (Fig. 1 and 2). Increased amounts of benzaldehyde and benzoic acid were detected with anthrahydroquinone ion as the nucleophile. The level of production of benzaldehyde and benzoic acid was not sufficient, however, to account for the observed incomplete material balance. Similarly, when the adduct 5 was degraded, about 25% was converted to undetectable products.

The reversibility of the isomerization reaction was also investigated by examining the extent of formation of cis-cinnamic acid when trans-cinnamic acid (2) was heated at 195°C in basic solutions. Less than 1% was converted to 1 over an eight hour period. It was concluded that the back conversion of 2 to 1 during the reactions of compound 1 was insignificant.

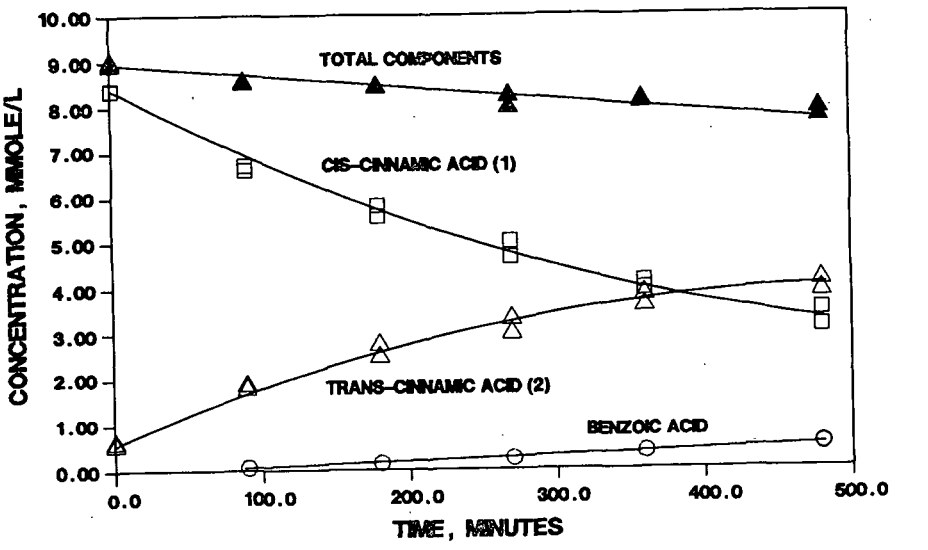


Figure 3. Mass balance for the reaction of 1 in 0.435M and 0.118M AHQ at 195°C.

Kinetic Treatment

The following pseudo-first-order rate expression was assumed based on the employment of a large excess of reagent (nucleophilic) relative to reactant concentration.[17]

$$d[R]/dt = -k_r [R] \quad (5)$$

where [R] = reactant concentration, mol L^{-1}

k_r = pseudo-first-order rate constant for reactant disappearance, s^{-1}

Integration and rearrangement results in:

$$\ln [R] = -k_r t + \ln [R]_o \quad (6)$$

where $[R]_o$ = initial reactant concentration, mol L^{-1}

Pseudo-first-order rate constants for the disappearance of reactant were calculated from Eq. 6 using a least squares regression technique. Pseudo-first-order kinetics were verified by showing that the reaction followed Eq. 6 over two half lives (Fig. 4).[17]

When using more than one nucleophile, the pseudo-first-order rate constant determined in Eq. 6 is defined as in Eq. 7.

$$k_r = k_{HO} [HO^-] + k_{Add} [Add] \quad (7)$$

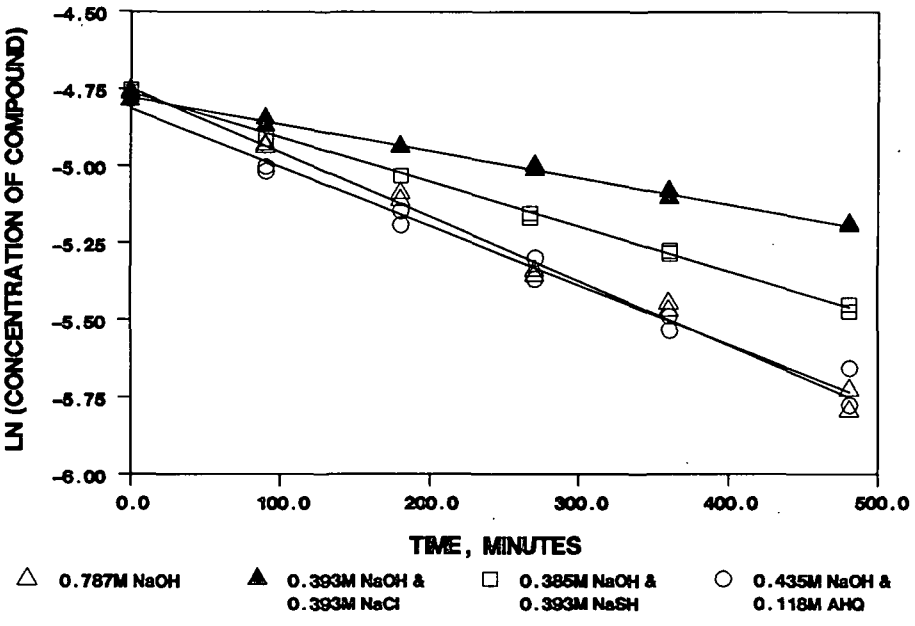


Figure 4. Pseudo-first-order reactions of 1 under the above conditions at 195°C.

where k_{HO} = rate constant associated with hydroxide ion, s^{-1}

$[HO^-]$ = concentration of hydroxide ion, mol L^{-1}

k_{Add} = rate constant associated with the additive, s^{-1}

[Add] = concentration of additive, mol L^{-1}

The rate constants for each additive were calculated from Eq. 7.

General Reaction Conditions

Compound 1 was heated in oxygen-free aqueous solutions which contained hydroxide, hydrosulfide, and anthrahydroquinone ions. Excesses of each reagent were used so that their concentrations remained essentially constant, which allowed use of pseudo-first-order rate expressions. The ionic strength of the medium was held constant when possible to minimize its effects on the rate constant. The reactions of 1 were extensively studied at 195°C, although the reaction at 171°C was briefly investigated to determine the effect of temperature on nucleophilic order.

Hydroxide Reactions

Data from three isomerizations of cis-cinnamic acid (1) in 0.787M sodium hydroxide solution at 194°C were used to determine the rate constant associated

with hydroxide ion. Data were analyzed using Eq. 6 to determine the observed rate constant (Fig. 4); the average value for k_{HO}, was calculated to be 4.30 (± 0.30) x 10^{-5} sec^{-1}. [The error limits stated for the rate constants represent the 95% confidence interval.]

The hydroxide ion concentration was varied (0.79M versus 0.39M) to verify the reaction order.[17] Sodium chloride was added to maintain a constant ionic strength. Using the observed rate constants from these reactions (Fig. 4), the reaction order was calculated to be 1.2. The reaction was, therefore, assumed to be first-order.

Hydrosulfide and Related Sulfur Compound Reactions

Data from three isomerizations of 1 in a solution containing 0.385M sodium hydroxide and 0.393M sodium hydrosulfide at 195°C were used to determine the rate constant associated with hydrosulfide ion. The data (Fig. 4) were analyzed using Eq. 7 to determine the observed rate constant. The average value for k_{HS} was 1.88 (± 0.46) x 10^{-5} $sec.^{-1}$ Propagation of errors led to relatively large confidence intervals around the k values for the additives.[18]

Analysis of the sulfide solution used in these reactions showed there were 6% sodium sulfite, 2% sodium thiosulfate, and 0.6% sodium sulfate impurities. Of prime importance was the level of sulfite and thiosulfate ions. These ions are known to have nucleophilicities similar to that of hydrosulfide ion.[2]

Separate 195°C reactions of 1 with sodium sulfite (0.0881M) and sodium thiosulfate (0.0890M), in the presence of 0.870M sodium hydroxide, were then investigated. Analysis of the data showed both sulfite and thiosulfate ions were more reactive than hydrosulfide and hydroxide ion (Table 1). The large errors associated with the k values are due to having only one degree of freedom to determine the standard error. The high reactivity of sulfite and thiosulfate toward unsaturated carbon centers has previously not been reported. The effect of these species (which would be present in pulping liquors) on the degradation of quinonemethides may be of some importance.

TABLE 1

Reaction Rate Constants of 1 at 195°C.

Reagent	Rate constant x 10^5, sec-1
SO_3^{-2}	23.0 ± 4.2
$S_2O_3^{-2}$	10.1 ± 8.7
HS^-	1.9 ± 0.5
HO^-	4.3 ± 0.3

The reactivity of hydrosulfide and sulfite ions was further investigated to determine the reaction order of these species as well as to test their additive effects (Table 2). Thiosulfate ion was not tested because its concentration in the sulfide solutions and rate constant were less than those of sulfite ion. Compound 1 was heated at 195°C under conditions shown in Fig. 5. Rate constants were calculated using the rate constant for hydroxide ion of 4.30 x 10^{-5} sec^{-1} (Table 1).

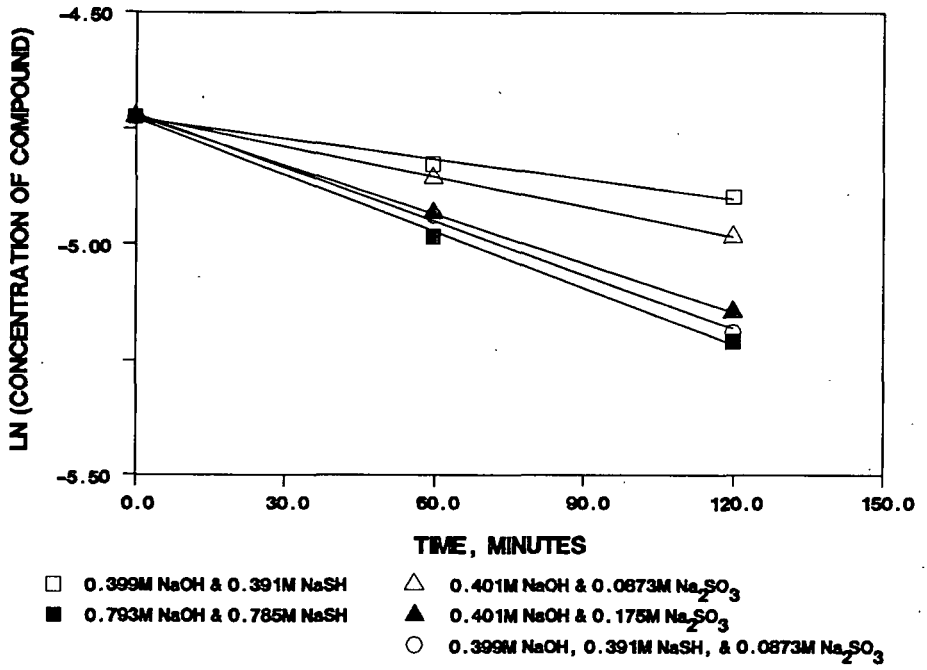


FIGURE 5. Comparison of reaction rates for 1 at 195°C under the above conditions.

TABLE 2

Rate Constants for the Degradation of 1 at 195°C with Different Reagents.

Reagents (molarity)			Rate Constants x 10^5 (sec^{-1})	
NaOH	NaSH	Na_2SO_3	k_{HS}	k_{SO_3}
1.04	0.176	-	5.49	-
0.523	0.523	-	2.60	-
0.399	0.391	-	1.58	-
0.793	0.785	-	4.14	-
0.401	-	0.0873	-	20.4
0.401	-	0.175	-	23.1
0.399	0.391	0.0873	6.92	22.2*

*Average of two values.

The reaction order for sulfite ion was first-order based on the two observed rate constants. Changes in the concentrations of hydroxide or sulfite did not alter the rate constant. The rate constant was unusually high when both hydrosulfide and sulfite were present in significant quantities. This synergism between hydrosulfide and sulfite ions has been previously noted.[19]

The rate constants from the reactions of hydrosulfide ion, however, were not constant and appeared to vary with changes in the hydroxide concentration. At first, we thought that the equilibrium between HS^- and S^{-2} (Eq. 4) was being shifted toward the sulfide ion at high hydroxide ion concentrations and that S^{-2} was more effective at promoting cis to trans-cinnamic acid isomerization. The equilibrium constant (K_2) associated with sodium sulfide production from sodium hydrosulfide is not well understood under these conditions.[20] Even using a wide range of K_2 values, from 10^{-12} to 10^{-17}, we could not explain the observed kinetic data.

Inclusion of a second hydroxide ion term in the kinetic expression to describe the rate of isomerization of cis-cinnamic acid in the presence of hydrosulfide ion gives the following relationship between the observed rate constant and specific rate constants:

$$k_r = k_{HO}\,[HO^-] + k_{HO-HS}\,[HO^-]\,[HS^-] \qquad (8)$$

The rate constant k_{HO-HS} was determined using Eq. 8 and the data in Table 2. The values of k_{HO-HS} (Table 3) appear to be constant over the range of reaction conditions. Variations appear to be dependent on the experimental error rather than true differences. The experimental error is propagated through each manipulation giving large confidence intervals in the final result.

TABLE 3

Determination of k_{HO-HS} Over Specified Reaction Conditions.

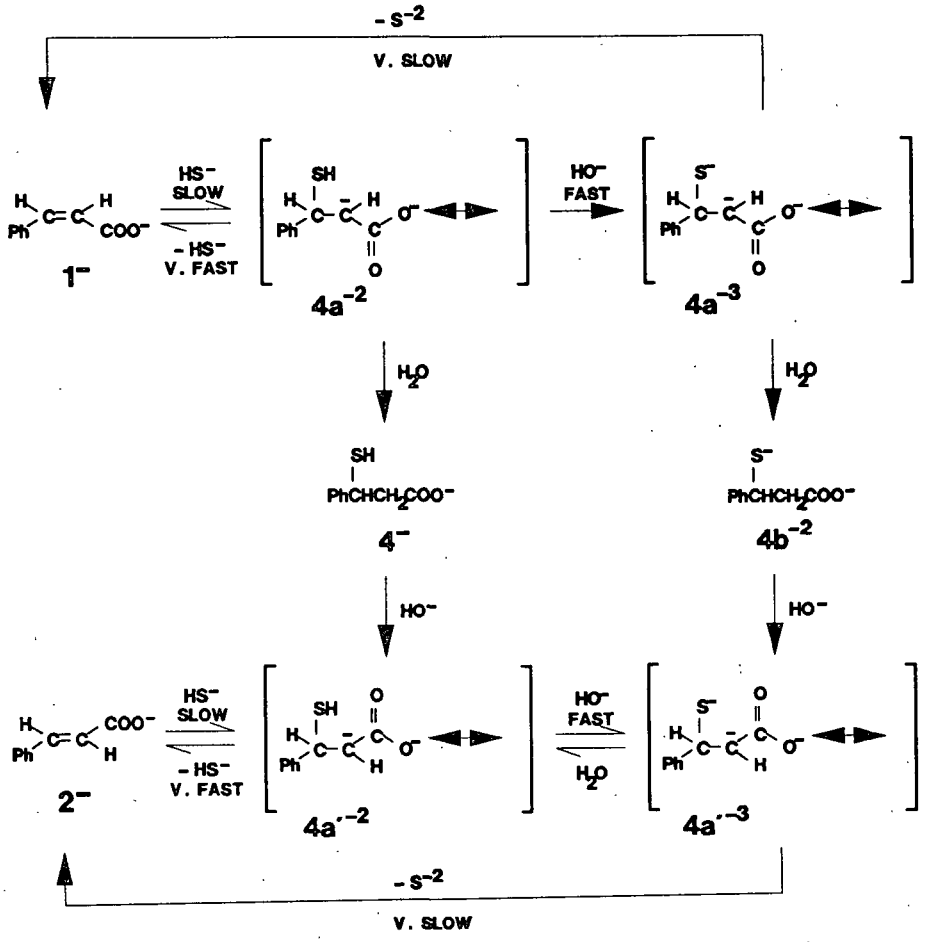
10^5 k_r (sec^{-1})	NaOH (M)	NaSH (M)	10^5 k_{HO-HS} (M^{-2} sec^{-1})
5.57 ± 0.21	1.06	0.175	5.46 ± 2.84
3.69 ± 0.07	0.536	0.523	4.94 ± 0.82
2.39 ± 0.08	0.385	0.393	4.85 ± 1.29
2.28 ± 0.06	0.385	0.393	4.13 ± 1.16
2.52 ± 0.06	0.385	0.393	5.71 ± 1.16
2.35 ± 2.66	0.399	0.391	4.07 ± 17.8
6.70 ± 2.53	0.793	0.785	5.29 ± 4.45

The reaction scheme shown in Scheme 2 was postulated as a possible explanation for the increased cis to trans isomerization rate with HS^- at higher hydroxide concentrations. Addition of HS^- to the carbon-carbon double bond was assumed to be a relatively slow step. The reverse reaction, $\mathbf{4a}^{-2}$ to 1^-, is probably very fast since hydrosulfide ion is a good leaving group. If the reverse reaction is much faster than C_α-C_β bond rotation or protonation/deprotonation ($\mathbf{4a}^{-2} \longrightarrow \mathbf{4a'}^{-2}$), little isomerization will occur. If the adduct $\mathbf{4a'}^{-2}$ is ionized by hydroxide ion, the lifetime of the resulting adduct $\mathbf{4a}^{-3}$ should increase substantially because the leaving ability of S^{-2} would be much less than that of HS^-.[1] In addition, the trianion, $\mathbf{4a}^{-3}$ should be preferentially protonated at C_α, rather than the sulfur, leading to $\mathbf{4b}^{-2}$ and eventually to trans-cinnamic acid.

Anthrahydroquinone Reactions

Data from four degradations of 1 in solutions containing approximately 0.44M sodium hydroxide and 0.12M anthrahydroquinone were used to determine the rate constant associated with anthrahydroquinone ion. The data were analyzed using Eq. 7 to determine the observed rate constant (Fig. 4). The average value for k_{AHQ} was 9.03 (± 3.80) x 10^{-5} sec^{-1}.

SCHEME 2



The effect of hydroxide ion concentration on the apparent rate constant associated with anthrahydroquinone ion was also examined. Analysis of the data (Fig. 6) showed that the reaction order of AHQ^{-2} was approximately one. The rate constant associated with anthrahydroquinone ion, however, increased with increased hydroxide ion concentration.

The rate constants and relative rate constants associated with the isomerization of cis- to trans-cinnamic acid with hydroxide, hydrosulfide, and anthrahydroquinone ions are shown in Table 4. Since the observed rate constants for HS^- and AHQ^{-2} are influenced by hydroxide ion concentration, which differs somewhat for the Table 4 entries, the relative rate constants for HS^- and AHQ^{-2} are somewhat higher than shown. Hydrosulfide and anthrahydroquinone ions appear

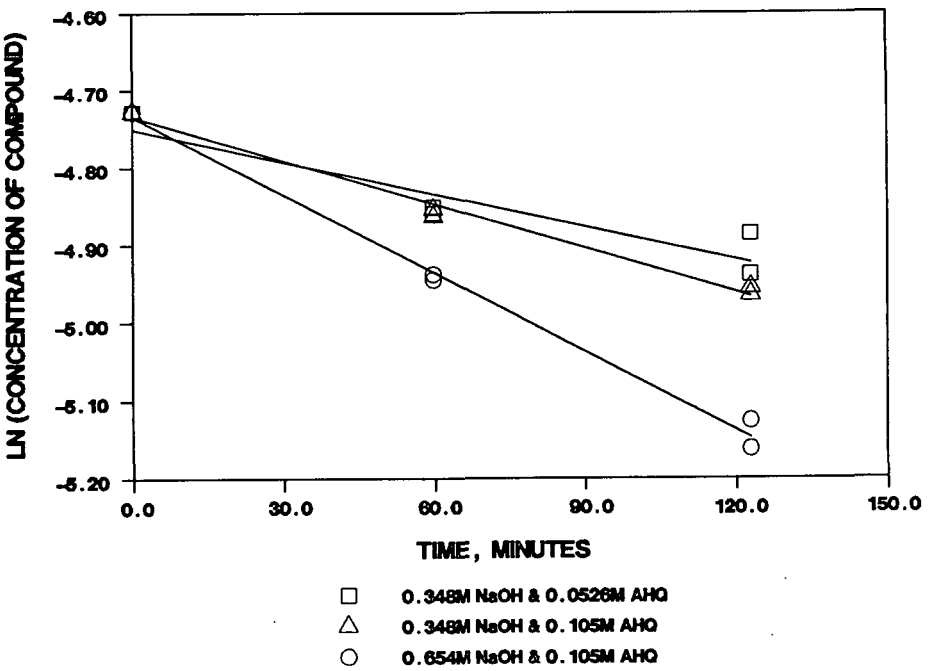


FIGURE 6. Comparison of observed reaction rates at 195°C when concentrations of hydroxide and anthrahydroquinone ions are varied: □, 0.348 M NaOH and 0.0526 M AHQ; Δ, 0.348 M NaOH and 0.105 M AHQ; ○, 0.654 M NaOH and 0.105 M AHQ.

to add to the double bond at a greater rate than that measured by isomerization. Based on the relative rate constant and entire set of data, anthrahydroquinone ion still appears to be the most reactive species toward unsaturated carbon centers, followed by hydroxide and hydrosulfide ions, which have similar nucleophilic strength.

TABLE 4

Reaction Rate Constants of 1 at 195°C.

Nucleophile	10^5 k, sec^{-1}	k_{rel}
NaOH	4.3	1.0
NaSH	1.9	0.4
Na_2AHQ	9.0	2.1

Isomerization Rates at 171°C

Rate constants for the isomerization of 1 to 2 at 171°C were also determined (shown in Table 5) under conditions similar to the degradations described in Table 4. The relative nucleophilic order ($AHQ^{-2} > HO^- > HS^-$) did not change by lowering the reaction temperature. The relative strength of hydrosulfide and anthrahydroquinone ions increased, which may suggest that hydroxide ion was more

solvated at 171°C. If the data in Tables 4 and 5 were extrapolated to lower temperatures, a change in nucleophilic order for HO^- and HS^- may exist.

TABLE 5

Reaction Rate Constants of 1 at 171°C.

Nucleophile	10^6 k, sec^{-1}	k_{rel}
NaOH	7.56	1.0
NaSH	6.77	0.9
Na2AHQ	22.9	3.0

CONCLUSIONS

The addition-elimination reactions at an unsaturated carbon center for cis-cinnamic acid should be similar to reactions at C_α of quinonemethides, which are key intermediates in pulping. The driving force behind the reaction of cis-cinnamic acid is formation of the more thermodynamically stable trans-isomer, a gain of approximately 3-7 kcal/mol.[21] On the other hand, the driving force behind quinonemethide addition (Eq. 1) is aromatization of the benzene ring, a gain of approximately 36 kcal/mol.[1] The quinonemethide, therefore, should be much more reactive.

Based on the observed nucleophilicities with cis-cinnamic acid, anthrahydroquinone ion should be a very reactive species with quinonemethides; this fact may in part account for its high effectiveness as a pulping additive. Hydroxide and hydrosulfide ions would appear to compete for quinonemethides at near equal levels, while sulfite and thiosulfate ions may have reactivities similar to that of anthrahydroquinone ion.

EXPERIMENTAL

Melting points were determined on a Thomas Hoover capillary melting point apparatus. Infrared (IR) spectra, referenced against polystyrene, were obtained using sodium chloride discs on a Perkin-Elmer 700 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Jeol FX100 Fourier transform spectrometer at 40°C. Mass spectroscopy (MS) was performed on a Hewlett-Packard 5985 instrument interfaced to a gas chromatograph. Separation by GC was typically performed on OV-17 (3%) on Chromosorb W HP (100-120 mesh) in glass tubing (6 ft x 2 mm) rigged for on-column injection. Electron impact (EI) MS

utilized helium as the carrier gas (30 mL min^{-1}), a source temperature of 200°C, an ionizing voltage of 70 eV, and the GC-MS interface of 250°C.

cis-Cinnamic Acid (1). The title compound was prepared as previously described[15] using hydrogen gas to yield a white crystalline solid: m.p. 58-60.5°C, (lit.[22,23] 54-56°C, 67.5-68.0°C); IR (mull) cm^{-1} 3750 (O-H), 1950, 1880, 1810 (Ar-H overtones), 1690 (C=O), and 1630 (C=C); ^{1}H-NMR (DMSO-d_6) δ 5.96 (d, J = 12.8 Hz, 1, Ph-CH=CH-COOH), 6.89 (d, J = 12.8 Hz, 1, Ph-CH=CH-COOH), 7.26-7.64 (m, 5, aryl-H), and 12.41 (br s, 0.7, COOH); ^{13}C-NMR (DMSO-$_6$) ppm 120.9 (d, Ph-CH=CH-COOH), 127.8, 128.5, 129.3 (aryl-C), 134.7 (s, C_1), 140.1 (d, Ph-CH=CH-COOH), and 167.1 (s, COOH); MS m/z (%) 148 (65, M^+), 147 (100), 131 (16), 103 (40), 102 (19), 91 (20), 77 (31), and 51 (15).

3-Hydroxy-3-phenylpropionic Acid (3). Ethyl 3-hydroxy-3-phenylpropionate[24] (5.0 g, 26 mmol) was refluxed in 5% potassium hydroxide solution for 4.5 hours. The product mixture was acidified with 6M hydrochloric acid, extracted into diethyl ether, dried and evaporated. The resulting solid was recrystallized from water to yield 3.3 g (77%) of white solid: m.p. 89.5-91.0°C (lit.[25,26] 92-93°C, 93-94°C); IR (mull) cm^{-1} 3300 (O-H) and 1700 (C=O); ^{1}H-NMR (DMSO-d_6) δ 2.55 (d, J = 7.0 Hz, 2, CH_2), 4.96 (t, J = 6.8 Hz, 1, CH), 5.30 (br s, 0.6, OH), 7.1-7.4 (m, 5, aryl-H), and 11.95 (s, 0.7, COOH); ^{13}C-NMR (DMSO-d_6) ppm 44.5 (t, CH2), 69.5 (d, CH), 125.6, 126.7, 127.9 (aryl-C), 144.7 (s, C_1), and 171.9 (s, COOH); MS m/z (%) 166 (43, M^+), 107 (100), 79 (70), 77 (53), and 51 (14).

3-Mercapto-3-phenylpropionic Acid (4). The procedure of Apfeld and Dimmel[27] was modified to produce the title compound. Ethyl 3-hydroxy-3-phenylpropionate (4.0 g, 21 mmol), thiourea (1.7 g, 23 mmol), and concentrated hydrochloric acid (10 mL) in water (100 mL) were refluxed with stirring for 49 hours. The mixture was then refluxed for an additional six hours following the addition of 50% sodium hydroxide solution (10 mL). The mixture was acidified after cooling, extracted into diethyl ether, dried and evaporated to yield an odorous white solid. Recrystallization from water gave 1.81 g (45%) of 4 : m.p. 90-100°C (lit.[28] 109°C); IR (mull) cm^{-1} 1710 (C=O); ^{1}H-NMR and ^{13}C-NMR were in accord with the expected structure and showed the presence of some minor impurities; MS m/z (%) 182 (27, M^+), 149 (41), 107 (100), 79 (24), 77 (30), 51 (12), 45 (11). GC-MS of a diazomethane-treated sample showed the presence of desired dimethylated product. No attempt was made to further purify the solid.

10-Hydroxy-10-(1-phenyl-3-carboxypropyl)-9(10H)-anthracenone Lactone (5). 10-Hydroxy-10-(1-phenyl-3-oxopropyl)-9(10H)-anthracenone hemiacetal[29] (252 mg, 0.737 mmol) was dissolved in acetone (10 mL). A chromic acid solution was prepared by dissolving sodium dichromate dihydrate (242 mg, 0.814 mmol) in water (5 mL) containing concentrated sulfuric acid (0.15 mL, 2.7 mmol). This solution was added to the acetone solution over a period of 15 minutes and then stirred for an additional 21 hours. The resulting mixture was diluted with water, extracted into diethyl ether, dried and evaporated to yield the desired product as a tan solid: m.p. 206-209°C; IR (mull) cm^{-1} 1780 (lactone carbonyl), 1660 (carbonyl), 1600 (aromatic); ^{1}H-NMR (DMSO-d_6) δ 3.06 (d of d, J = 8 and 17 Hz, 1, CH-CH$_{cis}$H$_{trans}$), 3.56 (d of d, J = 13, 17 Hz, 1, CH-CH$_{cis}$H$_{trans}$), 4.03 (d of d, J = 8, 13 Hz, 1, CH-CH$_{cis}$H$_{trans}$), 6.22 (d, J = 7 Hz, 2, C_2' and C_6'-H), 6.89 (t, J = 7 Hz, 2, C_3' and C_5'-H), 7.05 (t, J = 7 Hz, 1, C_4'-H), 7.4-8.2 (m, 8, aryl-H);[30] ^{13}C-NMR (DMSO-d_6) ppm 32.1 (CH_2), 57.4 (CH), 85.4 (C_{10}), 124.7, 125.8, 126.4, 126.7, 127.5, 127.7, 128.8, 128.9, 130.2, 130.7, 132.7, 132.9, 133.1, 134.3, 134.4, 139.3, 143.0 (aryl-C), 175.4 (lactone C), 181.0 (anthracenone C);[30] MS m/z (%) 340 (10, M^+), 104 (100).

cis-Cinnamic Acid Isomerization. The isomerization experiments were carried out in a series of 4-mL capacity pressure vessels (bombs) as previously described.[15] The bombs were filled with appropriate amounts of reactants and sealed in a nitrogen atmosphere. Sodium hydroxide solutions were prepared using oxygen-free water from ultrapure sodium hydroxide solution (30%) (Alfa Products). Sodium sulfide solutions were prepared from reagent grade sodium sulfide nonahydrate dissolved in oxygen-free water and stored under nitrogen. Anthrahydroquinone solutions were prepared by reducing anthraquinone in a nitrogen atmosphere using sodium dithionite.[31] The resulting product was dissolved in aqueous sodium hydroxide, filtered, and stored under nitrogen. Aqueous solutions were prepared such that after dilution in the bombs, the reaction solution contained 0.01M model compound.

The bombs were placed in a preheated oil bath and then removed after the desired reaction times. The bomb contents were worked up and analyzed as previously described.[15] The GC retention times were: benzaldehyde, 1.9 min; methyl benzoate, 3.2 min; phenylacetic acid methyl ester (internal standard), 4.4 min; methyl hydrocinnate acid, 5.7 min; methyl cis-cinnamate, 6.3 min; and methyl trans-cinnamate, 7.4 min.

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REFERENCES

1. March, J. Advanced Organic Chemistry: Reactions, Mechanisms and Structure, 2nd ed., McGraw-Hill, New York, 1977.
2. Swain, C. G.; Scott, C. B. J. Am. Chem. Soc. 1953, 75, 141.
3. Edwards, J. O.; Pearson, R. G. J. Am. Chem. Soc. 1962, 84, 16.
4. Pearson, R. G. J. Am. Chem. Soc. 1963, 85, 3533.
5. Klopman, G. J. Am. Chem. Soc. 1968, 90, 223.
6. Parker, A. J. Chem. Rev. 1969, 69, 1.
7. Bohme, D. K.; Mackay, G. I.; Payzant, J. D. J. Am. Chem. Soc. 1974, 96, 4027.
8. Olmstead, W. N.; Brauman, J. I. J. Am. Chem. Soc. 1977, 99, 4219.
9. Asubiojo, O. I.; Brauman, J. I. J. Am. Chem. Soc. 1979, 101, 3715.
10. Bohme, D. K.; Mackay, G. I. J. Am. Chem. Soc. 1981, 103, 978.
11. Gierer, J. Holzforschung 1982, 36, 43.
12. Dimmel, D. R.; Shepard, D. J. Wood Chem. Technol. 1982, 2, 73.
13. Dimmel, D. R. J. Wood Chem. Technol. 1985, 5, 1; and subsequent articles in the series.
14. Noyce, D. S.; King, P. A.; Kirby, F. B.; Reed, W. L. J. Am. Chem. Soc. 1962, 84, 1632.
15. Reed, G. A.; Dimmel, D. R. J. Org. Chem., article in this issue.
16. Blythe, D. A.; Schroeder, L. R. J. Wood. Chem. Technol. 1985, 5, 313.
17. Moore, J. W.; Pearson, R. G. Kinetics and Mechanism, 3rd ed.; John Wiley and Sons: New York, 1981, p. 37-82.
18. Meyer, S. L. Data Analysis for Scientists and Engineers, John Wiley and Sons, New York, 1977, pp. 39-48.
19. Olm, L.; Teder, A. Sv. Papperstidn. 1986, 89(16), 20.
20. Gonthier, Y.; Marchand, D.; Renaud, M. Sv. Papperstidn. 1983, 86, R113.
21. Crombie, L. Q. J. Chem. Soc. 1952, 6, 101.
22. Chaloner, P. A. J. Chem. Soc., Perkin Trans. 2 1980, 1028.
23. Noyce, D. S.; King, P. A.; Kirby, F. B.; Reed, W. L. J. Am. Chem. Soc. 1962, 84, 1632.

24. Rathke, M. W.; Lindert, A. J. Am. Chem. Soc. 1970, 35, 3966.

25. Cohen, S. G.; Weinstein, S. Y. J. Am. Chem. Soc. 1964, 86, 725.

26. Noyce, D. S.; Lane, C. A. J. Am. Chem. Soc. 1962, 84, 1635.

27. Apfeld, P. B.; Dimmel, D. R. J. Wood Chem. Technol. 1982, 2, 269.

28. Tanaka, H.; Yokoyama, A. Chem. Pharm. Bull. 1961, 9, 66.

29. Dimmel, D. R.; Shepard, D. J. Org. Chem. 1982, 47, 22.

30. Analysis performed by Spectral Data Services, Inc., Champaign, IL.

31. Smith, D. A. Doctoral Dissertation, The Institute of Paper Chemistry, Appleton, WI, 1986.